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Effect of Carboxymethyl Cellulose Binder on the Quality of Biomass Pellets

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ABSTRACT: Quality and energy efficiency are two critical concerns associated with the production of biomass pellets. This study elaborates methods to improve the quality of biomass pellets by using a new additive solution (carboxymethyl cellulose (CMC)) and its influence on pellet physical and mechanical properties during the densification of three types of agricultural waste (cotton stalks, wheat straw, and rape straw). Simultaneously, the cohesion and binding mechanisms were analyzed with attenuated total reflectance infrared spectra (ATR-FTIR) and light microscopy (LM). The results show that adding CMC lowers the energy consumption and increases the pellet quality by improving relaxed density, compressive strength, and durability for cotton stalks and wheat straw. However, adding CMC to rape straw decreased the pellet quality. Our results showed that addition of CMC leads to electrostatic forces among the particles that might be responsible for the cohesion strength of biomass pellets, which may be attributed to the formation of polyelectrolytes. The electric dipole from water molecule in biomass and OH groups on the CMC formed the hydrogen bond. In addition, strong bonds, similar to solid bridges, were formed at the interfaces between CMC and biomass solid particles. These interactions enhance interparticle bonding in the pellets, thereby improving the product quality and providing an efficient means to convert agricultural waste into biomass energy.

1. INTRODUCTION

Biomass, as a renewable energy and CO_2-neutral source, has been attracting widespread attention.[1−3] Being a large agricultural country, China annually produces a large quantity of agricultural waste, which can be used to produce a large share of biomass fuel.[4,5] However, because of low energy density, low bulk density, and irregular shape and size, it is very difficult to store and transport biomass in its original form, which increases the utilization costs.[6,7] Additionally, the direct on-site burning of agricultural waste not only causes the energy waste due to the lack of efficient use of energy, but also significantly contributes to air pollution (airborne particulate matter, PM).[4,8] Therefore, highly efficient, low cost, and environmentally friendly biomass utilization technology is needed to meet the country's enormous energy demand. One of the most effective ways to address these problems is to convert biomass waste into pellets or briquettes. Densification can effectively lead to the desired shape and increase the energy density of biomass, making it convenient to transport, store, and utilize the biomass. Moreover, biomass pellets/briquettes can be widely used in industrial boilers for pyrolysis, gasification, direct combustion, or cofiring with coal.[9,10]

Because agricultural waste has different types and characteristics, many countries have made extensive efforts to improve the quality of biomass pellets/briquettes.[6−13] Due to the huge production quantity annually produced in China, agricultural residue and waste are often densified into pellets/briquettes in the same way as wood pellets;[12] however, the compressive strength and durability of agro-pellets is lower than that densified from wood. This is because fibrous materials of agricultural waste are elastic, demonstrating springback properties, while wood, which is rich in lignin, has a low softening temperature.[14] Stelte et al.[15] showed that the density of straw pellets increases greatly with pelletizing pressure, while pressure of more than 250 MPa has a limited effect on density. Gilbert et al.[16] found high bonding characteristics of pellets when the pelletizing temperature is increased. Some studies pointed out that the optimum moisture content is in the range 12−23% for straw pellets.[9,15,17,18] Other researchers found that the smaller the particle size of raw biomass material is, the better the compression is.[9,19−22]

Other than optimizing operating parameters, the physical properties of biomass pellets might also be effectively improved by adding the binders to raw material.[23] Traditional binders usually include both organic materials (e.g., lignin, proteins, and starch)[24−26] and inorganic materials (e.g., bentonite and hydrated lime).[27,28] Ahn et al.[29] found that the coffee meal not only increases pellets durability, but also its calorific value. Pfost et al.[28] has reported that the durability of animal feed pellets increases by 1.5−2.5% when 2.4 wt % of bentonite is added. Tabil et al.[27] proved that alfalfa pelleted with $Ca(OH)_2$ exhibits more desirable qualities and effectively reduces pelletization energy consumption. Larsson et al.[26] found that the durability of spruce pellets increases on adding different amounts of cassava stem powder and potato starch as binders. Some researchers also found that some biomass residues could be considered as binders to enhance the strength of the biomass pellets.[5,19,30]

However, some binders may cause environmental pollution when added to biomass to produce pellets. Moreover, most binders are commonly restricted to pellets production of feed and pyrolytic biochar.[9,24,29] Therefore, it is very important to make sure that a binder is environmentally friendly and cost-

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effective, along with being of high quality and energy efficient. Carboxymethyl cellulose (CMC) is a cellulose derivative containing carboxymethyl groups. Because adjacent CMC chains repel each other owing to the electrostatic repulsion of molecules that extend in aqueous solution and which can form a colloidal solution with high viscosity, CMC is commonly used as a binder while producing food, medicines, common chemicals, petroleum, paper, textiles, and construction materials.[31,32] Some studies have reported that CMC is also used as a high viscosity binder for coal briquettes or granular activated carbon.[33,34] Its use in the densification of biomass, however, is seldom researched. When CMC is used in low proportions (<5% by weight) in a CMC solution, it results in a cost-effective (compared to starch and lignin power) and environmentally friendly solution. Therefore, this study investigates CMC as an additive for the densification of biomass and focuses on the pellet quality which refers to relaxed density, compressive strength, durability properties, and energy consumption. Simultaneously, the bonding mechanism was intensively explored using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and light microscopy (LM).

2. EXPERIMENTS AND METHODS

2.1. Materials and Binder. Typical agricultural waste materials, including cotton stalks, wheat straw, and rape straw, were selected as biomass samples and were collected from Central China. The raw agricultural waste materials (65−110 cm long) were ground with a hammer mill (C11-34, CHYUN TSEH INDUSTRIAL, Taiwan) into several smaller pieces, then further smashed to fragments smaller than 40 mesh (0.63 mm), and dried at 105 °C for 24 h.

The CMC used for this study was of analytical purity and purchased from Sinopharm Chemical Reagent Co., Ltd., China. About 5 wt % of CMC was added to deionized water to prepare the solution and form a colloidal suspension, which was used as a binder for densification.

2.2. Equipment and Pelletizing Processing. Densification was conducted on a universal material testing machine (WDW3200, Kexin Corporation, China) with a mold for the feedstock and CMC solution as shown in Figure 1. The mold equipment includes a cylindrical die

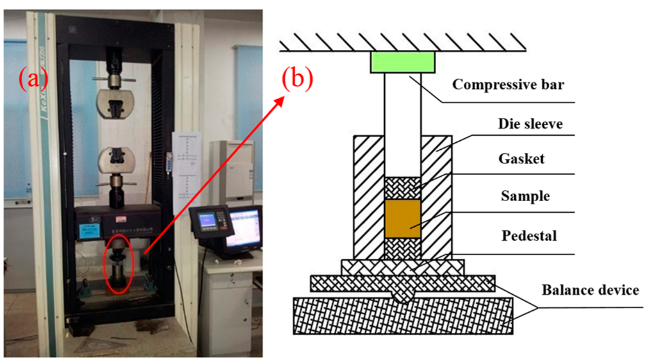

Figure 1. Schematic of compression system: (a) the mechanical press machine and (b) the piston mold.

(20.5 mm in diameter and 80 mm in length), a piston (20 mm in diameter and 71 mm in length), two gaskets (20 mm in diameter and 9 mm in length), and a pedestal. The values of pressure and displacement were recorded online.

The CMC solutions and water were added into the biomass samples for densification. On the basis of the limitation[9] and cost of the binders added, the biomass feedstock and CMC solutions were mixed with weight ratios of 100/0, 99.5/0.5, 99/1, and 98.5/1.5. The adding method of CMC solutions and water into the biomass samples for densification was as follows. First, CMC solution of the corresponding volume was added into 3.5 g biomass samples using a transfer liquid gun, followed by being thoroughly stirred to make sure a homogeneous mixing. About 15% (w/w) of water was then added into the mixture (mixed with biomass and CMC) and stirred for 24 h at ambient temperature with a magnetic stirrer. The addition of extra water can enhance the bond strength of pellets, not only due to increasing the van der Waals' forces between particles,[35] but also promoting the further dissolution of CMC. Approximately 4.2 g of the final mixed sample was put into the cylindrical mold to make a single pellet of 20 mm in diameter and 10 mm in length using a velocity of 10 mm/min until the compressive displacements reached the desired value (ensure the length of pellet is 10 mm), then held for 30 s, and released promptly. The pellets were ejected from the other end of the mold by the compression tester at a compression rate of 5 mm/min. For each trial, the die was rinsed with acetone and wiped clean when the biomass feedstock was changed.

2.3. Energy Required. For biomass pellet preparation, the energy consumption is a critical factor.[36] The energy consumption was obtained at the sample pelletization phase, which included compression and ejection of a single pellet. It can be calculated with eq 1

$$W = \sum_{i=1}^{n} F_i S_i \tag{1}$$

where W (J) is the energy consumption of the biomass pellets during the compression and ejection process; F_i and S_i are the pressure (N) and displacement (m) of pellets, respectively.

2.4. Physical Characteristics of Biomass Pellets. Particle density, compressive strength, and durability comprise what are considered the physical and mechanical properties of the biomass pellets. At least three replicates were performed for each condition, and the standard deviations were calculated. The particle densities of the pellets include the maximum compression density (ρ_m) and relaxed density (ρ_r). Parameter ρ_m was measured as soon as the pellet was ejected from the die, while ρ_r was measured after keeping the pellet for 1 week.

The compressive strength of the biomass pellets was tested using a cylindrical metal probe of 20 mm diameter. Each pellet was placed individually in a horizontal direction in a universal material testing machine (WDW3200, Kexin Corporation, China) with a compression rate of 2 mm/min until the pellet was crushed.[14]

The durability of biomass pellets was tested using 30 pellet samples, which were densified using the three aforementioned biomass types with the CMC solution, by placing them in a 2 mm sieve where they were vibrated for 30 min. Next, the tumbled pellets were weighed, and the final mass was recorded. The durability (I, %) was calculated using eq 2[37]

$$I = 100 - (m_i - m_f)/m_i \times 100\% \tag{2}$$

where m_i (g) and m_f (g) are the initial and final masses of the samples, respectively.

2.5. ATR-FTIR and Light Microscopy Analysis. To analyze the functional group changes of the pellet surfaces that determined the bonding characteristics of the pellets,[38] a Fourier transform infrared spectrometer (VERTEX 70 FT-IR, Bruker Corporation, Germany) with an ATR accessory (SPECAC Corporation, Germany) was used to record the ATR-FTIR spectra at the ambient temperature. In order to obtain the best experimental results, a metal rod was used against the pellet surfaces with a certain amount of pressure (1000−1500 Pa) before the test. All spectra were recorded with 128 scans for the background (air) and the pellets in a range 4000−2400 cm^{-1} with 4 cm^{-1} resolution.

The cross-section image of biomass pellets was measured using light microscopy (Axiovert 200MAT, Carl Zeiss Light Microscope, Germany). Five measurements were performed for each sample, and the image was amplified to 500 μm to observe the structure of the adjacent particles.

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3. RESULTS AND DISCUSSION

3.1. Physicochemical Characteristics of Raw Biomass Material. Table 1 presents the properties of raw biomass samples. Biomass samples showed higher volatile content but lower heat value and lower energy density than coal. This indicates that densification is necessary for scale utilization of biomass resources. Since S and N contents in these biomass samples are very low, they have the potential to be used as environmentally friendly fuel materials. With respect to the three biomass samples, regarding the inherent property of each plant, cotton stalks showed the highest cellulose and lignin content and were very hard: it demonstrated similar properties to wood materials. Wheat straw presented the highest hemicellulose content. Rape stalk showed the highest extractive content but the lowest lignin content. The variant property of biomass materials might play some role on each type's pelletizing behavior and potential utilization. Due to the low energy density, low bulk density (shown in Table 1), and poor adhesive force of the agricultural waste, it is necessary to compact these raw materials into biomass pellets with binders in order to increase the energy density of these biomass materials.

Table 1. Properties of the Raw Materials

analysis	cotton stalks	wheat straw	rape straw
Proximate Analysis[b] (wt %, d)			
ash	4.84 (0.36)	12.91 (0.87)	6.84 (0.29)
fixed carbon	16.54 (1.42)	14.19 (0.69)	15.39 (0.84)
volatile matter	78.62 (4.19)	72.90 (3.82)	77.77 (5.63)
Ultimate Analysis[b] (wt %, d)			
C	47.24 (1.97)	42.69 (1.38)	44.42 (2.22)
H	6.34 (0.31)	5.74 (0.40)	7.06 (0.16)
N	1.67 (0.08)	0.57 (0.04)	0.88 (0.03)
O*[a]	39.80 (1.46)	37.68 (2.34)	40.27 (2.26)
S	0.36 (0.01)	0.41 (0.01)	0.53 (0.01)
Chemical Analysis[b] (wt %, d)			
cellulose	43.22 (4.02)	38.56 (2.99)	37.23 (3.17)
hemicellulose	26.28 (2.24)	37.44 (3.15)	23.47 (1.96)
lignin	26.42 (0.94)	17.32 (1.07)	14.13 (0.84)
extract content	3.24 (0.23)	4.78 (0.64)	10.67 (1.57)
HHV[c] (MJ/kg)	17.92	15.65	16.70
energy density[b] (GJ/m^3)	3.30 (0.27)	2.22 (0.38)	2.44 (0.44)
bulk density[b] (ρ_b) (kg/m^3)	184 (8)	142 (14)	146 (12)

[a]O* was calculated by difference; d = dry basis. The value of standard deviation is shown in parentheses. [b]n = 2. [c]n = 1.

Given the natural irregularities of the raw materials and the reduced influence of particle size on the physical characteristics of the biomass pellet, particle size variations need to be minimized for densification. Biomass particle size was analyzed using a laser particle size analyzer (Master Min, MALVERN, Britain); the particle size distribution is shown in Figure 2. It can be seen that it is very difficult to grind biomass particles, and that size mostly remains over 100 μm. Although cotton stalks are somewhat harder than the other two biomass samples, it is easy to grind, and its particle sizes are also smaller (average size = 230.821 μm). In contrast, wheat straw and rape stalk are larger, with the average size between 374.49 and 388.43 μm.

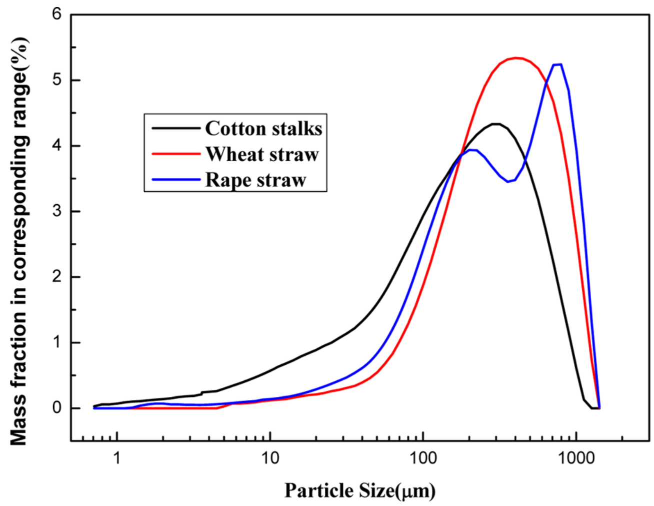

Figure 2. Raw material particle size distribution of cotton stalks, wheat straw, and rape straw.

3.2. Pelletization Behavior of Biomass Particles. The density changing profile of biomass particles during the compression process is plotted in Figure 3. It was observed that the density of the pellets increases with the compression pressure increasing, especially when it increased rapidly in low pressure (0−10 MPa). However, when the density reached 1300 kg/m^3, the compression became very difficult, and the extent of the density increase was lowered. The maximum density of the biomass pellets is likely an upper limit for that of the plant cell wall, which has been determined to be ~1400 kg/m^3;[39] therefore, the closer its density approached the cell wall density, the smaller the extent of its density increased with increasing pressure.[15] Moreover, the fiber elasticity of the raw biomass material for densification resulted in the springback, which made it difficult to reach the maximum density value. When the pressure reached 70 MPa, the density of all of the pellets meets the requirement of commercial pellets.[9,40] In addition, under the same compression pressure, the binder sample (cotton stalks and wheat straw) experienced a larger compression density compared to the no-binder sample, and they all increased with an increase in CMC content; the increasing trends of density variation, however, differed for variant biomass types with compression pressure at 0−5 MPa.

With respect to cotton stalks with the CMC solution addition (Figure 3a), these pellets were revealed to be different in density when mixed with feedstock in the initial compression. Before they reached 400 kg/m^3, these pellets showed a rapid increase in density, which is attributable to the loose structure of the raw material. At this stage of compression, interparticle air is squeezed out of the raw material, and the particles are rearranged becoming densely packed while still keeping their own characteristics (Figure 7).[21] Once density passes 400 kg/m^3, however, it shows a linear relationship with the CMC content under the same pressure. The growth rate of the pellet density is greater when the amount of CMC is 1.5 wt %, with the maximum compression pressure decreasing by 63.1% for cotton stock pellets, indicating that cotton stalks are more sensitive to CMC in the compression process, and that a high proportion of CMC can effectively improve pellet quality. Wheat straw (Figure 3b) displayed a similar trend as that of cotton stalks; however, the increase of density of the former is much lower than that of the latter. Moreover, no obvious difference was observed in the binder pellets when the CMC content is increased until their

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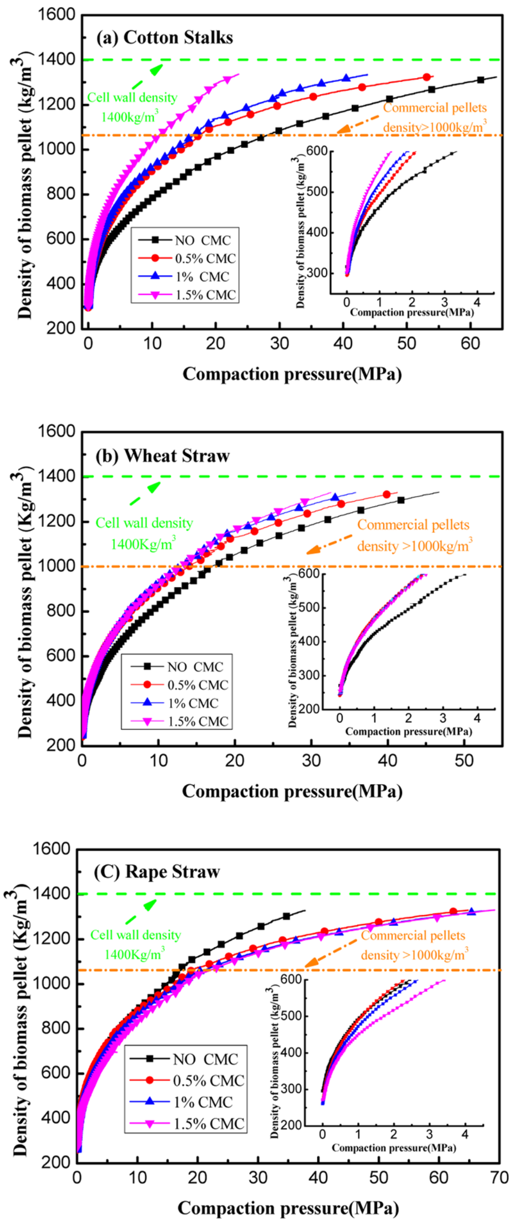

Figure 3. Density of single pellet of feedstock material at different CMC dosage: (a) cotton stalks, (b) wheat straw, (c) rape straw. (The densified pellets were prepared from biomass powder mixed with CMC solution by a densification machine in a cylindrical mold under ambient temperature and pressures lower than 70 MPa.)

density reached 1000 kg/m^3. Subsequently, a gradual increase in pellet density was seen with increasing the CMC content after the compression pressure was increased to more than 15 MPa. Because wheat straw has a lower bulk density (Table 1) than cotton stalks, pellet density of the former had higher sensitivity to compression pressure than to CMC content at the initial compression process, but subsequently, the CMC still dominated and could be used as a binder for densification of wheat straw. For example, the maximum compression pressure decreased by 30.3% for wheat straw pellets when the amount of CMC was 1.5 wt %. Overall, for the pellets of cotton stalks and wheat straw, CMC as the targeted source of cellulosic fiber is the only adhesive component in the mixture, and it played a major role during the compression process. As higher adhesion function was generated due to CMC adhering to the surface of the biomass particles, it resulted in lower operation pressure for densification.[35] In addition, it showed that pellets with binders can reach the desired value of the pellet density (1 kg/m^3) when they were under lower pressure.[41]

Regarding rape stalk, the density of these pellets can easily reach 1366 kg/m^3 without a binder, but with a binder, the compression process was ineffective, and the addition of CMC did not play a positive role in the compression. Furthermore, the compressing pressure increased on increasing the CMC amount. This result might be linked to the oleophobic properties of the CMC, increasing the repulsion between the particles. Therefore, in order to obtain higher density, more compression pressure is needed.[7]

3.3. Physical Properties of Biomass Pellets.

Relaxation Density and Pellet Expansion. A higher quality usually means a higher relaxed density for the pellets. Table 2 shows the maximum compression density (ρ_m), relaxed density (ρ_r), and longitudinal and diametric expansion of the biomass feedstock with a binder. Table 1 shows that the bulk density of biomass feedstock was very low, from 142 to 184 kg/m^3, and that wheat straw consisted of the lowest bulk density and cotton stalks the highest. Through densification, the maximum compression density of pellets with and without a binder both increased significantly, and reached 1323−1336 kg/m^3. It was also proven that densification can effectively increase biomass density while simultaneously solving the problem of biomass transportation, storage, and handling.[9,35,42]

After densification, the pellets were stored for 1 week, during which time the fiber elasticity resulted in springback causing volume expansions of the pellets, lowering their density. Consequently, the diametric and longitudinal expansion of the biomass pellets has an important impact on pellet quality. The calculations revealed an obvious growth in the longitudinal direction but only a small diametric expansion; typical compression pressure is conducted in an axial direction of the pellet during the compression process, therefore explaining the re-expansion pattern. That is why the cotton stalk pellet sample's longitudinal expansion (20%) was much higher compared to its diametric expansion (0.6%). By adding

Table 2. Maximum Compression Density (ρ_m), Relaxed Density (ρ_r), and Expansion (%) of the Pellets with Binders[a]

CMC content (w/w)	max compression density[b] (ρ_m) (kg/m^3)	.ongitudinal expansion[b], %	diametric expansion[b], %	relaxed density[b] (ρ_r) (kg/m^3)
		Cotton Stalk		
0%	1323 (12)	28.8 (1.3)	0.6 (0.2)	1015 (14)
0.5%	1327 (19)	20.8 (1.6)	0.2 (0.1)	1094 (17)
1%	1335 (28)	18.9 (1.2)	0.4 (0.1)	1114 (13)
1.5%	1336 (23)	16.6 (0.9)	0.4 (0.2)	1137 (24)
		Wheat Straw		
0%	1332 (14)	31.0 (2.5)	0.8 (0.3)	1001 (25)
0.5%	1331 (29)	22.7 (1.9)	0.7 (0.1)	1070 (19)
1%	1330 (22)	20.5 (2.7)	0.4 (0.2)	1095 (29)
1.5%	1330 (20)	17.9 (3.1)	0.5 (0.3)	1117 (36)
		Rape Straw		
0%	1328 (21)	35.8 (4.2)	0.4 (0.2)	970 (34)
0.5%	1329 (31)	57.2 (5.0)	0.8 (0.3)	832 (32)
1%	1327 (38)	60.3 (4.9)	1.1 (0.4)	810 (24)
1.5%	1330 (50)	67.3 (5.4)	0.9 (0.3)	781 (29)

[a]The value of standard deviation is shown in parentheses. [b]n = 5.

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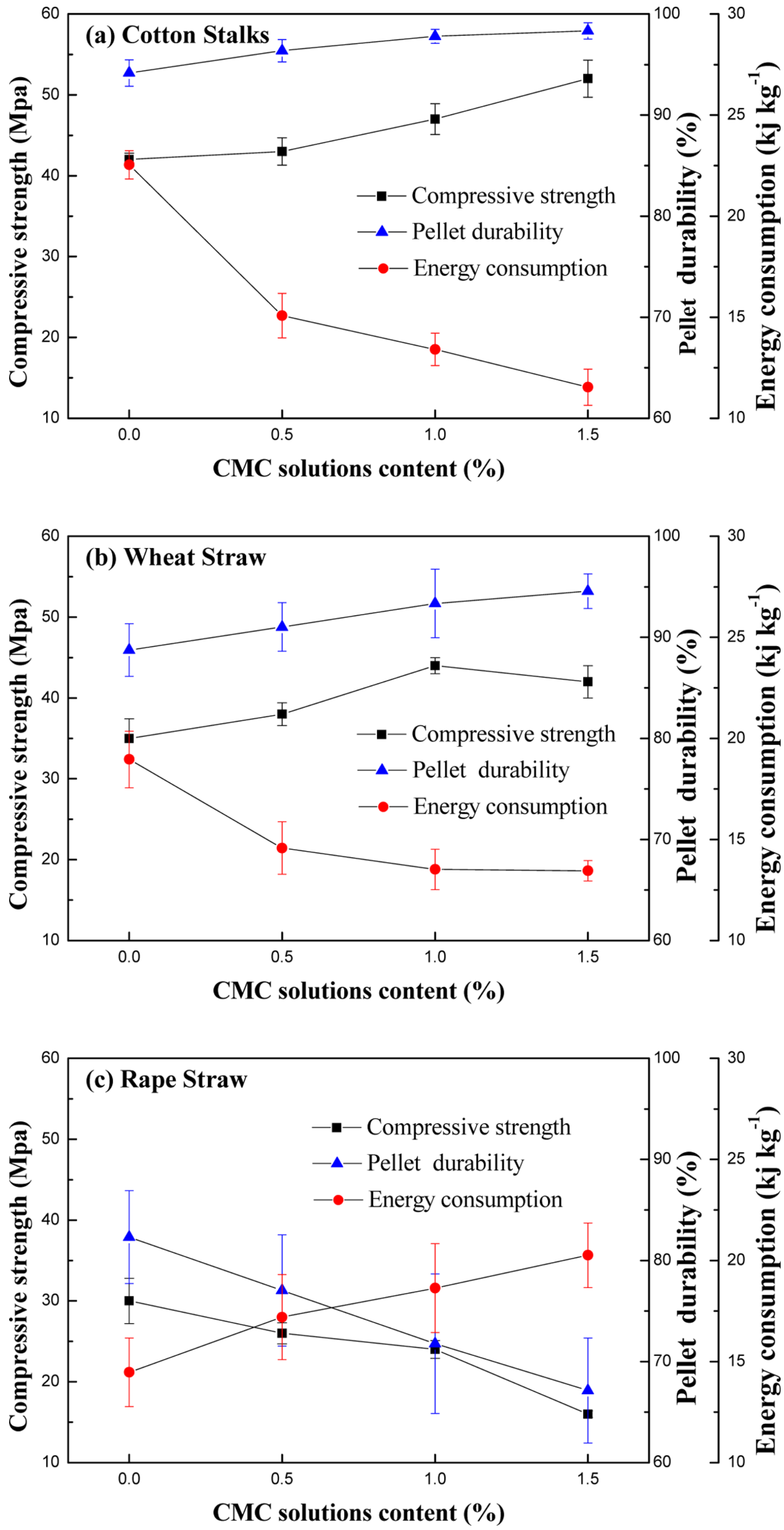

Figure 4. Effect of CMC content on the qualities of pellets: (a) cotton stalks, (b) wheat straw, (c) rape straw.

CMC, the longitudinal and diametric expansion of the pellets was decreased greatly, and decreased with increasing binder content. It was also implied that the relaxed density of a pellet using a binder is much higher than that without a binder. In particular, for pellets densified with a CMC content of 1.5 wt %, the longitudinal and diametric expansion decreased by 42.4% and 33.3%, respectively; its relaxed density increased by 12.0% and reached the highest value of 1137 kg/m^3. Wheat straw pellets showed a similar trend for relaxed density, but at a much lower rate than that of the cotton stalks pellet. Its relaxed density increased by approximately 6.4%−11.6% with CMC content from 0.5% to 1.5 wt %, and the highest relaxed density

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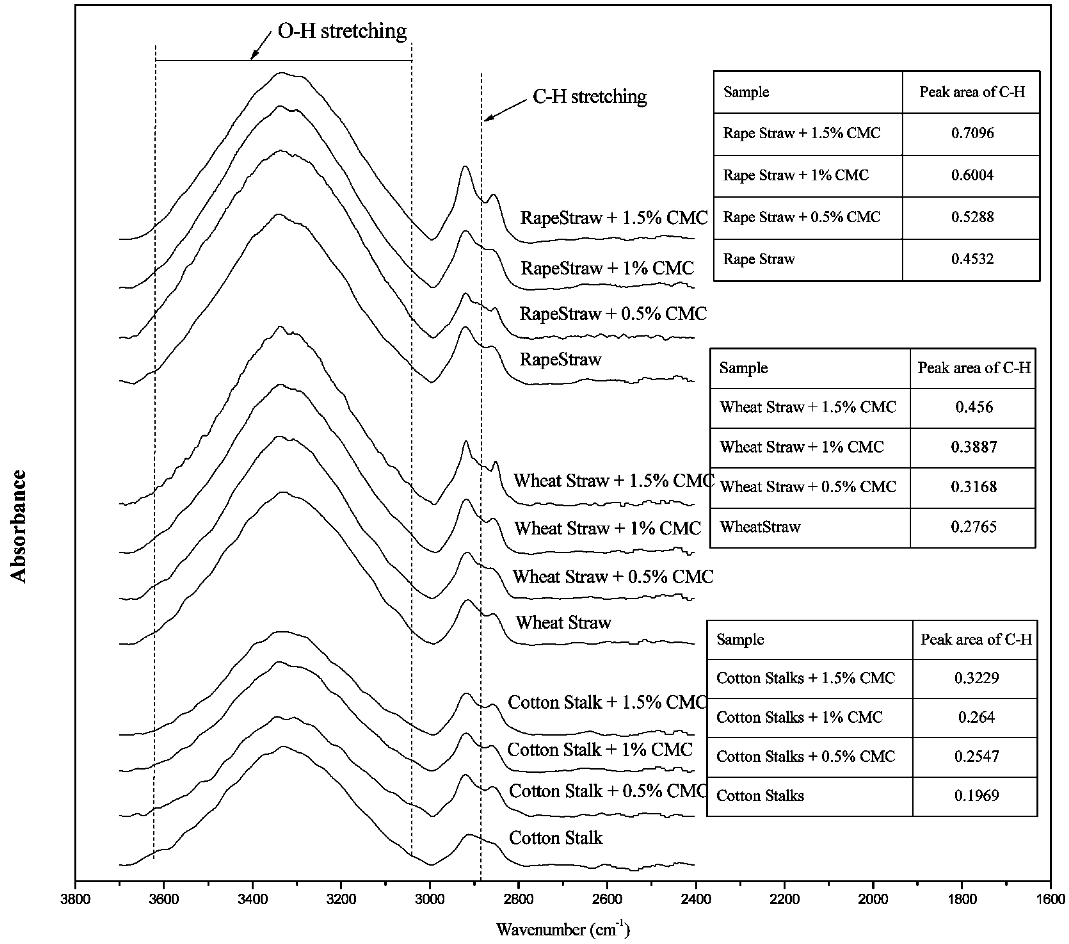

Figure 5. ATR-FTIR spectra of the pellets surface.

was 1117 kg/m^3 when CMC content was 1.5 wt %. In addition, its longitudinal and diametric expansion decreased by a range 26.8–42.3% and 12.5–50.0%, respectively. Moreover, even when the smallest amount of binder content (0.5 wt %) was added, the relaxed density still achieved commercial pellet density (1000–1120 kg/m^3). It was possible to ensure more contact with the CMC, strengthening the bonding between adjacent particles, and thereby resulting in a decreased springback in the pellets. Hence, CMC can be considered to be an effective binder to increase the relaxed density of pellets, reduce the volumetric expansion, and significantly improve pellet quality.

However, rape straw exhibited a different trend: volumetric expansion increased when CMC content was increased, and it was observed that the structure of the rape straw pellets became looser with the binder. Its longitudinal and diametric expansion increased to 67.3% and 0.9%, respectively, and density was reduced largely to a range between 781 and 970 kg/m^3, which is significantly lower than that of the pellets without CMC. On the basis of these observations, it was concluded that the addition of CMC did not play a positive role on rape straw densification. This may be related to the high extract content (10.7%) of rape straw, and the fact that the extractive contains a high content of waxes rich in long chain fatty acids, which would hinder the viscosity effect of the binder, and increase its degree of swelling to a certain extent.[43]

Compressive Strength. Compressive strength tests on the pellets are displayed in Figure 4. For cotton stalks (Figure 4a), the pellets made with a binder showed a higher compressive strength compared to that densified without CMC; overall, this type of pellet exhibited an increase in compressive strength in proportion with the increase of the CMC content in the binder solution. The highest compressive strength was 52 MPa for cotton stalks when CMC binder content was 1.5 wt %. Wheat straw (Figure 4b), however, did exhibit a different trend in that when the CMC content was less than 1 wt %, the wheat straw pellets' compressive strength increased with an increase in CMC content, but when CMC content exceeded 1 wt %, its compressive strength decreased. This implies that, for wheat straw compression, only a limited proportion of CMC may be added to effectively increase compressive strength before it produces countereffects. Rape straw (Figure 4c), however, required inversely proportional concentrations of CMC solution, with ranges from 0.5% to 1.5 wt %. The compressive strength of rape straw pellets was significantly reduced by 13.33–46.67%. Its low compressive strength is usually a result of its large void structure and gaps between internal particles; further confirmation will be discussed on the basis of the analysis of images from the light microscopy in Figure 6i–l. Furthermore, the extractive in biomass materials might present another critical issue regarding densification, as these materials were expelled during the compressing process, which limited the hydrogen bonding between adjacent particles, which is attributed to the CMC characteristics of the expelled waxes that are abundant in rape straw (Table 1). Hence, rape straw is very difficult to compress and CMC had the reverse effect.

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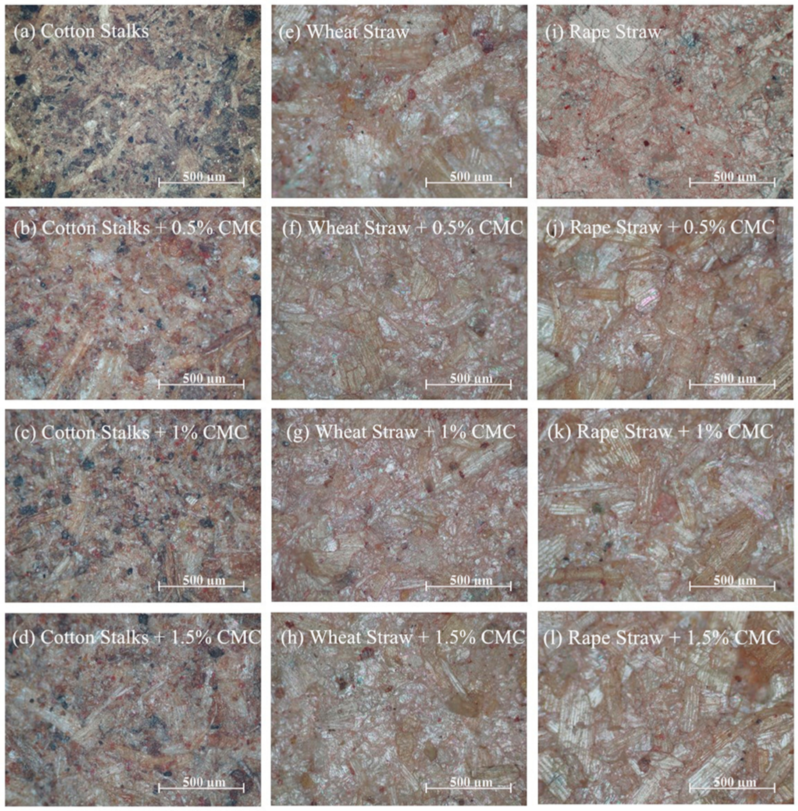

Figure 6. Light microscopy (LM) (magnification at 500 μm) images of pellets: (a–d) cotton stalk pellets and cotton stalk pellets with CMC, (e–h) wheat straw pellets and wheat straw pellets with CMC, (i–l) rape straw pellets and rape straw pellets with CMC.

The compressive strength showed a close relation to biomass type. For pellets densified without a binder, the compressive strength was rated in the following order: cotton stalks > wheat straw > rape straw. These findings might be attributed to the variance of lignin content that affects the cohesive force of whatever substances are acting as a natural binder on increasing compressive strength.[44]

Durability. The effect of CMC on pellet durability is also presented in Figure 4, which illustrates that the durability trend of pellets (both compressed by feedstock and feedstock with CMC solution) is similar to their density (including compression density and relaxed density). The durability of biomass pellets (cotton stalks and wheat straw) increased with the proportion of CMC increasing. Higher relaxation density would lead to greater adhesive force between adjacent particles owing to the adhesiveness of CMC. Therefore, durability improved with the addition of CMC. For rape straw, the durability of the pellets densified with a binder is less than 80% of those densified without a binder, which did not meet commercial standards, and thus it is concluded that CMC is not a suitable binder for rape straw densification.

Energy Consumption. Figure 4 presents the effect of CMC content on energy consumption during the compression of biomass pellets. Miao et al.[45] pointed out that binders would harden the feedstock particles and cause an increase in energy input. However, different results showed that the CMC content had an obvious effect for cotton stalks: when CMC content increased from 0 to 1.5 wt %, cotton stalk pellets required only half as much energy, with their energy consumption significantly decreasing from 22.54 to 11.54 kJ/kg. Wheat straw exhibited a similar trend with its energy consumption for pellets decreasing by 23.1% to 29%. No discernible decrease, however, was observed when the binder content exceeded 1 wt %. This indicates that an optimizing amount of binder needs to be selected for biomass pelletization in respect to the energy cost during the densification process. In view of these results, the addition of CMC led to lower pellet energy input for cotton stalks and wheat straw. Rape straw, however, consumed more energy when CMC content was increased. Thereby, the bonding mechanism of the pellets with CMC addition should be discussed further.

3.4. Surface Structure of Biomass Pellets. The ATR-FTIR spectroscopy of biomass pellet surfaces is shown in Figure 5. The bands in the diagram are of pellet surfaces at 2850 and 2920 cm^{-1}, which reflect the stretching of the C–H bonding, showing a strong link between hydrophobic extractives such as waxes and oils.[14] Hence, here the peak area was calculated to investigate the change of C–H bond groups with a semiquantitative method. From Figure 5, it can be seen that the pellets of cotton stalks and wheat straw without a binder (0.1969 and 0.2765, respectively) show very limited C–H stretching. When a binder is added, however, the value increases greatly, indicating a large amount of C–H stretching. The surfaces of densified pellets with binders are coated by a cuticle, rich in low molecular weight wax.[15] This can be explained by the fact that oils and waxes belonging to low molecular weight hydrocarbons are repelled by CMC and migrate to the pellet surfaces during the pellet compression process. This phenomenon is favorable for reducing frictional force between the raw material and the mold,[15] and leads to the reduction of pelletization energy consumption as shown in Figure 4.

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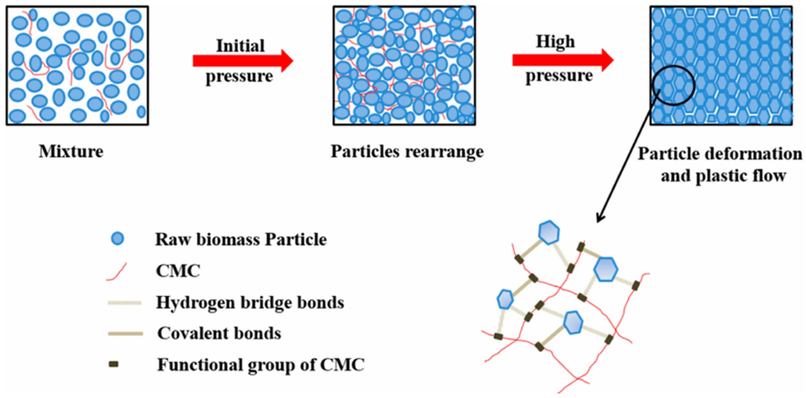

Figure 7. Binding mechanism of biomass raw added CMC solution during compress process.

For rape straw, the wax peak area also showed a substantial increase after adding the CMC solution. However, a contrary result appeared for rape straw, where adding the binder made the compression process difficult. It might be explained by the fact that while rape straw showed greater extractive content, the wax, which is rich in extract, migrated from the biomass cells to the surface of the pellet, resulting in greater energy requirements for compression. The required energy is larger than that caused by the frictional force decrease, and it was especially found that the higher the CMC content was, the more energy was required (Figure 4).

The images of the light microscopy of biomass pellets fracture surfaces are shown in Figure 6. From the surface pictures of cotton stalks and wheat straw pellets without binders (Figure 6a,e), interparticle gaps between adjacent particles show a poor cohesive force. This could indicate a lower relaxed density but larger expansion ratio of cotton stalks and wheat straw pellets without a binder. The uniform and flat surface showing for biomass pellets (cotton stalks and wheat straw) with CMC solution, and interparticle distance, however, is very limited, and furthermore, there was no evidence of the springback phenomenon between particles. It is likely that the CMC flows and fills in gaps between adjacent particles, bonding solid particles to each other with the cooling/drying of the pellets; hence, the adjacent particles had a good bonding effect and made the pellet much stronger.[9] It can be inferred that CMC as a binder adds to the biomass materials, acting as a binding component between particles. It is mainly due to CMC, which belongs to the polyelectrolyte category; being applied to the small particles, they become captured and connected by electrostatic forces. Meanwhile, the hydrogen bond is formed by electric dipoles between the water molecules in the biomass and OH groups on the CMC.[46] In addition, strong bonds, similar to solid bridges,[35] are formed by interaction between $-OCH_2COOH$ groups on the CMC and OH groups in the biomass, where these interactions enhance interparticle bonding in the pellet.[47] Further, the binding mechanism of the raw biomass with the added CMC solution during the compression process is shown in Figure 7. In view of the good adhesion of biomass pellets compressed with a binder, this confirms that adding a CMC solution could lower expansion and enhance relaxed density, compressive strength, and durability of these pellets.

Rape straw pellets show no sign of adhesion function (Figures 6i–l). This might be due to the low lignin but high wax content (Table 1) occurring in the rape straw. van der Waals forces and some mechanical interlocking are the primary mechanisms of bonding.[14] In addition, the wax content of rape straw is relatively high, and a weak chemical boundary layer is formed on the particle surface, resulting in low cohesive strength and poor interparticle bonding.[14] Nevertheless, due to the oleophobicity of CMC, it is not a favorable environment for the formation of bonds between the adjacent particles of the rape straw, and in fact the contact area between biomass particles is reduced. Simultaneously, the larger particle size also has some influence on its adhesion properties. It may also account for the poor quality of rape straw pellets after CMC is added. Therefore, in considering pellet properties, such as relaxed density, compressive strength, and durability, the research indicates that CMC was not a suitable binder for use in densification of biomass with high extractives.

4. CONCLUSIONS

In this study, the effect of CMC binders on physical and mechanical characteristic of biomass pellets was investigated. It was concluded as follows: (1) Attributed to the enhanced electrostatic forces, hydrogen bands and strong bonds formed at the surface of solid particles, when a CMC solution was added during the compression process of cotton stalks and wheat straw; these interactions significantly improved the quality of their pellets. Properties such as relaxed density, compressive strength, and durability exhibited a significant increase with an increase to CMC content; furthermore, the energy consumption was decreased with the increase of CMC content in these cases. (2) On the contrary, rape straw pellets, which are rich in extractives, exhibited lower quality properties when CMC was added compared to the condition when no CMC was added. This decrease in quality is mainly attributed to the oleophobic properties of CMC, a weak chemical boundary layer caused by high concentration of wax at the sample surfaces, reducing the adhesive force and van der Waals force between adjacent particles, and resulting in a low bonding effect and poor pellet quality; this was further verified by light microscopy (LM) images. Therefore, this finding indicates that CMC is not suitable as a binder for densification of biomass materials that are rich in extractives. (3) The high relaxed density, enhanced compressive strength, and desired durability of cotton stalks reached an optimum value of 1137 kg/m^3, 52 MPa, and 98.33% with 1.5 wt % CMC content added during densification. Wheat straw, however, reached its optimum value of these properties at 1095 kg/m^3, 54 MPa, and 93.35% when a 1 wt % content solution of CMC was added. These data sets are of critical use for commercial pelletization applications.

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Due to the environmental sustainability and cost-effectiveness of the study results, CMC is an effective binder for products being densified that contain minimal extractive content. In future studies, the function of a greater variety of types of binder content, moisture content, and particle size of biomass will be explored during densification experiments.

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Notes

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